Se ha comprobado que el incremento de ^{222}Rn en el aire del suelo se puede producir por dos mecanismos diferentes, tanto por el transporte directo por la corriente de CO_2 como por la generación en los ambientes superficiales al aumentar el contenido de los nucleídos padre (U/Ra) movilizados por el agua carbonatada, aunque este último efecto tiene que seguir evaluándose.

Los resultados demuestran que los valores alcanzados de ^{222}Rn en el aire del suelo pueden ser muy elevados, llegándose a obtener valores de hasta 430 $kBq \cdot m^{-3}$. Hecho que se tendrá que tener en consideración a la hora de realizar el análisis de riesgos de un proyecto de almacenamiento geológico de CO_2. Si las fugas se produjesen en zonas residenciales y se dan las condiciones para ello se podrían llegar a alcanzar concentraciones de riesgo en el interior de las viviendas. La ingesta de aguas afectada por las fugas de CO_2 podría ser otro peligro a tener en consideración, tanto por el aumento del ^{222}Rn transportado por la corriente de CO_2 como por la movilización de los nucleídos de uranio y radio favorecida por las aguas carbonatadas.

La relación del torón (^{220}Rn) con el flujo de CO_2 no es tan directa como con el radón (^{222}Rn), en este sentido en la emisión de gas seco de "La Sima" se detectó un claro descenso de la composición de ^{220}Rn al aumentar el flujo de CO_2 mientras que este efecto no se apreció, e incluso se produjo un ligero incremento al aumentar el flujo de CO_2, en los puntos de emisión asociadas con las surgencias de agua. Este hecho parece estar producido por la profundidad de origen de los isótopos del radón (^{222}Rn – ^{220}Rn), lo que confirmaría su utilización como trazador del origen de los gases, sin embargo se tiene que continuar investigando el origen exacto del radón para confirmar esta hipótesis.

1.4. Línea base de flujo de CO_2 en la PDT de Hontomín

Los valores de fondo de flujo de CO_2 desde el suelo a la atmósfera en la zona de la planta de desarrollo tecnológico que se va a construir en Hontomín, en el marco del proyecto Compostilla OXYCFB300, son bajos y semejantes a los valores típicos de origen biológico. Los valores medios están entre 4,9 y 13 $g \cdot m^{-2} \cdot day^{-1}$, menores a 18 $g \cdot m^{-2} \cdot d^{-1}$ que puede considerarse como un valor máximo de la media aritmética del flujo procedente de la respiración del suelo en la zona. No se detectaron evidencias de un origen profundo de CO_2 (por ejemplo, de los depósitos de hidrocarburo), lo que sugiere que la respiración del suelo es el único responsable de los valores de flujo de CO_2 observado en Hontomín.

También se realizaron mediciones en las zonas preferenciales de escape de gases desde profundidad, principalmente en los alrededores de los sondeos existentes (H-1, H-2, H-3 y H-4) y futuros (H-A y H-I) y en la zona de la falla sur (HNT3). El flujo de CO_2 en estas áreas es similar a los valores obtenidos en zonas sin vías preferenciales de escape de gases. Solo se detectaron algunos valores anómalos (alrededor de 40 $g \cdot m^{-2} \cdot d^{-1}$) en las inmediaciones del sondeo H-2, aunque estos valores no se pueden asociar inequívocamente a un origen profundo del CO_2 y es más probable que se deban a un incremento en la actividad biológica de la zona. Sin embargo, esta zona debe considerarse como un área de riesgo potencial para una fuga del CO_2 inyectado.

Los mayores valores de flujo de CO_2 se obtuvieron durante los periodos cálidos, como consecuencia de un incremento de la actividad biológica. Encontrándose además, los valores más altos de flujo de CO_2 en aquellas zonas donde la vegetación está más presente, zonas cultivadas y forestales. En Hontomín, el flujo de CO_2 es menor y homogéneo durante el invierno, mientras que en los meses cálidos es heterogéneo y mayor por el incremento de la actividad biológica.

La determinación de unos valores de referencia a partir de los cuales se puede considerar que se está produciendo una fuga desde el reservorio es de gran ayuda en los programas de monitorización y verificación durante la vida del proyecto CAC. Se calcularon dos grupos de valores de referencia de flujo de CO_2. El primero (UCL_{50}, 5 $g \cdot m^{-2} \cdot d^{-1}$) par zonas no aradas en los meses de otoño-invierno y 3,5 y 12 $g \cdot m^{-2} \cdot d^{-1}$ en primavera-verano para zonas aradas y no aradas, respectivamente. Estos valores pueden usarse como indicadores de un aumento en el flujo de CO_2 a modo de alarma para la detección de una posible fuga temprana. Si estos valores son superados, el monitoreo tienen que ser más exhaustivo y frecuente para evaluar la evolución de la posible fuga y de los riesgos asociados. El segundo grupo de valores de referencia (UCL_{99}) corresponde a 26 $g \cdot m^{-2} \cdot d^{-1}$ durante los meses de otoño-invierno en las zonas no aradas y 34 y 42 $g \cdot m^{-2} \cdot d^{-1}$ para los meses de primavera-verano en zonas aradas y no aradas, respectivamente. Superar la estimación del límite superior del percentil 99 puede considerarse como una evidencia de que la fuga de CO_2 se está produciendo.

1.5. Hidrogeoquímica de las aguas superficiales y de manantiales en el área afectada por la PDT de Hontomín

En este capítulo se analizan los primeros datos geoquímicos e isotópicos de las aguas superficiales (de escorrentía y de manantiales) de la zona de Hontomín-Huérmeces, lugar donde se colocará la Planta de Desarrollo Tecnológico de almacenamiento de CO_2, pudiéndose considerar como el valor de fondo (línea base). La composición química e isotópica indica que las aguas estudiadas, caracterizadas por valores de TDS relativamente bajos y una fácie hidrogeoquímica de $Ca^{2+}(Mg^{2+})$-HCO_3^-, están gobernadas por la aguas meteóricas con un circuito hidrogeológico superficial. A pesar de la detección de una fuente antropogénica de NO_3, dos aguas de manantial (Fuente Hontomin: FH3 y, en menor medida, Fuente Laguillo: LA1) muestran una posible contribución de aguas profundas, deducido por las concentraciones relativamente altas de As, B, Ba y U. En el Río Ubierna (RU8) se han encontrado características geoquímicas similares, deduciéndose también una hipotética entrada de agua salina (profunda) al río.

La química de las aguas principalmente está relacionada con los procesos de interacción de las aguas con las rocas de las unidades sedimentarias del área de HH, como son la disolución de los Ca(Mg)-carbonatos gobernados por la conversión del H_2CO_3 al ión HCO_3^-. De esta manera la calcita es la principal fuente de Ca, por su gran ratio de disolución en comparación con los Ca-silicatos y Al-silicatos (Marini, 2007). El contenido de $Ca^{2+}(Mg^{2+})$-HCO_3^- en las aguas es compatible con un sistema cerrado equilibrado con los minerales carbonatados. Se ha detectado una contaminación antropogénica significativa en las aguas de HH, llegándose a alcanzar valores particularmente altos de NO_3^- en algunos manantiales cercanos a la zona de inyección.

Por lo general, los gases disueltos en las aguas de HH están dominados por la componente atmosférica (N_2, O_2 y Ar). En algunos casos el gas predominante fue el CO_2, con unos valores isotópicos del carbono ($\delta^{13}C$-CO_2 y $\delta^{13}C$-TDIC) propios de una fuente biológica.

2. Trabajos futuros

Los trabajos futuros se centrarán en:

- Evaluar las técnicas de teledetección para identificar y cuantificar fugas de CO_2. Entre otros trabajos, el grupo de investigación formado por la UPM y la UniFi (Ortega et al., 2013) están realizando investigaciones, en análogos naturales, para evaluar la aplicabilidad de las imágenes multiespectrales e hiperespectrales en la detección de fugas.

- Analizar la aplicabilidad de otros gases en las técnicas de monitorización. La dificultad de detectar y diferenciar entre el CO_2 biológico y el procedente de una fuente profunda hace que sea necesario disponer del mayor número de datos posible que facilite esta labor. En este sentido otro gases, tales como el CH_4, H_2, N_2, Ar, He, pueden proporcionar información valiosa durante la interpretación de los resultados, sirviendo como trazadores naturales de una posible fuga de CO_2.

- Comparar, en diferentes escenarios, los métodos radiométricos para medir los isótopos de radón ($^{222}Rn/^{220}Rn$), evaluando las posibles diferencias existentes entre ellos. Considerando cuál (o cuáles) ofrecen mejor respuesta en las diferentes etapas de los proyectos de almacenamiento geológico de CO_2 (investigación, operacional, clausura y posterior a la clausura).

CAPÍTULO IV: BIBLIOGRAFÍA

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CAPÍTULO V: DIFUSIÓN DE RESULTADOS

1. Difusión de resultados

Los trabajos de investigación realizados durante la ejecución de la tesis doctoral han dado como resultado la publicación de 3 artículos en revistas internacionales[8] (Anexos 3, 4 y 5) y 19 comunicaciones en congresos. A continuación se realiza un listado de los más relevantes:

- **Artículos**

Autores: **Elío J.**, Ortega M.F., Chacón E., Mazadiego L.F., Grandia F.
Título: Sampling strategies using the "accumulation chamber" for monitoring geological storage of CO_2
Revista: International Journal of Greenhouse Gas Control
Volumen: 9
Páginas: 303-311
Año: 2012
ISSN: 1750-5836
Índice de Impacto (JCR-2012): 3,944 (Q1)

Autores: **Elío J.**, Nisi B., Ortega M.F., Mazadiego L.F, Vaselli O., Grandia F.
Título: CO_2 soil flux baseline at the Technological Development Plant for CO_2 injection at Hontomín (Burgos, Spain)

Revista: International Journal of Greenhouse Gas Control
Volumen: 18
Páginas: 224-236
Año: 2013
ISSN: 1750-5836
Índice de Impacto (JCR-2012): 3,944 (Q1)

Autores: Nisi B., Vaselli O., Tassi F., **Elío J.**, Delgado A., Mazadiego L.F., Ortega, M.F.
Título: Hydrogeochemistry of surface and spring waters in the surroundings of the CO_2 injection site at Hontomín–Huermeces (Burgos, Spain)

Revista: International Journal of Greenhouse Gas Control
Volumen: 14
Páginas: 151-168
Año: 2013
ISSN: 1750-5836
Índice de Impacto (JCR-2012): 3,944 (Q1)

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[8] Se han preparando otros dos artículos pendientes de enviar a revistas internacionales (ANEXO 6).

- **Congresos nacionales e internacionales**

Autores: **Elío J.**, Ortega M.F., Mazadiego L.F., Caballero J., Nisi B., Vaselli O., Grandía F., García M.J., Llamas J.F., García J.E.

Título: Monitorización y verificación de un almacenamiento geológico de CO2. Aplicación de la monitorización superficial en la PDT de Hontomín (Burgos, España)

Tipo de participación: Comunicación Oral

Congreso: XII Reunión del Grupo Español del Carbón (GEC2013)

Lugar de celebración: Madrid (España) Fecha: 20-23 de octubre de 2013

Autores: Rincones M.A., Ortega M.F., Elío J., Gutierrez del Olmo J., Mazadiego L.F., Iglesias L., García R., García M.J.

Título: Atmospheric and remote sensing surveys evaluated at the natural analogue "Campo de Calatrava" and its relation with isotopic Radon activity and CO2 flux as strategy for CCS projects

Tipo de participación: Comunicación Oral

Congreso: IX Congreso Ibérico - XI Congreso nacional de Geoquímica

Lugar de celebración: Soria (España) Fecha: 16-18 de septiembre de 2013

Autores: Ortega M.F., Rincones M., **Elío J.**, Gutiérrez Del Olmo J., Nisi B., Mazadiego L.F., Iglesias L., Vaselli O.

Título: Gas monitoring methodology and application to CCS projects as defined by atmospheric and remote sensing survey in the natural analogue of Campo de Calatrava

Tipo de participación: Comunicación Oral

Congreso: 13th International Conference on Environmental Science and Technology (CEST2013)

Lugar de celebración: Atenas (Grecia) Fecha: 5-7 de septiembre de 2013

Autores: Llamas B., Mazadiego L.F., **Elío J.**, Ortega M.F., Grandia F.

Título: Systematic approach to selection of technologies of monitoring in projects for geological storage of CO_2. Application of multiple criteria decision making

Tipo de participación: Comunicación Oral

Congreso: 13th International Conference on Environmental Science and Technology (CEST2013)

Lugar de celebración: Atenas (Grecia) Fecha: 5-7 de septiembre de 2013

Autores: Vaselli O., Nisi B., Tassi F., Darrah T., Bruno J., **Elío J.**, Grandia F., Del Villar LP.
Título: Gas discharges for continental Spain: geochemical and isotopic features

Tipo de participación: Comunicación Oral
Congreso: Goldschmidt 2013

Lugar de celebración: Florencia (Italia) Fecha: 25-30 de agosto de 2013

Autores: Nisi B., Vaselli O., Tassi F., **Elío J.**, Delgado Huertas A., Mazadiego L.F., Ortega M.F.
Título: Water chemistry at Hontomín-Huermeces (Burgos, Spain): insights for a pre-, intra- and post-CO_2 injection geochemical monitoring.

Tipo de participación: Comunicación Oral
Congreso: EGU General Assembly 2013.

Lugar de celebración: Viena (Austria) Fecha: 7 de abril de 2013

Autores: Grandía F., **Elio J.**, Mazadiego L.F., Ortega M.F., Llamas J.F.
Título: Rn Gas Emission Distribution in the Soil-Atmosphere Interface: Lessons Learned from CO_2 Storage Monitoring

Tipo de participación: Poster
Congreso: MoDeRn Monitoring in Geological Disposal of Radioactive Waste, objetives, strategies, technologies and public involvement

Lugar de celebración: Luxemburgo Fecha: 19 de marzo de 2013

Autores: **Elio J.**, Ortega M.F., Caballero J., García-González J.E., Nisi B., Vaselli O., Tassi F., Grandía F., Vilanova E., Mazadiego L.F., Gargía-Martínez M.J., Llamas J., Chacón E.
Título: Baseline of Soil CO_2 Flux in the Hontomin Site (Burgos, Spain)

Tipo de participación: Comunicación Oral
Congreso: 34th International Geological Congress

Lugar de celebración: Brisbane (Australia) Fecha: 5-10 de agosto de 2012

Autores: Nisi B., Vaselli O., **Elio J.**, Ortega M.F., Caballero J., Tassi F., Rappuoli D., Mazadiego L.F.
Título: CO_2 emission from two old mine drillings (Mt. Amiata, central Italy) as a posible example of storage and leakage of deep-seated CO_2

Tipo de participación: Comunicación oral
Congreso: 34th International Geological Congress

Lugar de celebración: Brisbane (Australia) Fecha: 5-10 de agosto de 2012

Autores: Mazadiego L.F., Grandia F., **Elio J.**, Nissi B., Vaselli O., Ortega M., Caballero J., Vilanova E., Chacón E., Llamas J.
Título: Baseline of Soil-Atmosphere CO_2 Flux in the Hontomin Site (Burgos, Spain)

Tipo de participación: Comunicación Oral
Congreso: Third EAGE CO_2 Geological Storage Workshop. Understanding the Behaviour of CO_2 in Geological Storage Reservoirs

Lugar de celebración: Edimburgo (Escocia) Fecha: 26-27 de marzo de 2012

Autores: Grandia F., Mazadiego L.F., **Elío J.**, Ortega M.F., Bruno J.
Título: Radon Isotope Measurements as a Monitoring Tool For CO2 Leakage in Geological Storage

Tipo de participación: Comunicación oral
Congreso: AGU fall meeting 2011

Lugar de celebración: San Francisco (EE.UU.) Fecha: 5 de diciembre de 2012

Autores: Mazadiego L.F., **Elío J.**, Nisi B., Ortega M.F., Caballero J., Vaselli O., Grandia F., Tassi F., Chacón E., Llamas J.
Título: Estudio de la línea base del flujo de CO_2 en Hontomín (Burgos).

Tipo de participación: Comunicación Oral
Congreso: II Coloquio Hispano-Francés sobre Almacenamiento Geológico de CO_2

Lugar de celebración: Ponferrada (España) Fecha: 24-26 de octubre de 2011

Autores: Grandia F., **Elío J.**, Ortega M.F., Caballero J., Nisi B., Vaselli O., Mazadiego L.F., Tassi F., Chacón E., García-González J.E., García-Martínez M.J., Llamas J., Vilanova E.
Título: Baseline of CO_2 fluxes in the PDT of Hontomín (Burgos, España)

Tipo de participación: Poster
Congreso: II coloquio Hispano-Francés sobre Almacenamiento Geológico de CO_2

Lugar de celebración: Ponferrada (España) Fecha: 24-26 de octubre de 2011

Autores: **Elío J.**, Ortega M.F., Caballero J., García-González J.E., Nisi B., Vaselli O., Tassi F., Grandia F., Vilanova E., Mazadiego L.F., García-Martínez M.J., Llamas J., Chacón E.
Título: Caracterización geoquímica de la línea base de flujo de CO_2 en la planta de almacenamiento geológico de Hontomín (Burgos, España).

Tipo de participación: Comunicación Oral
Congreso: VIII Congreso Ibérico de Geoquímica-XVII Semana de Geoquímica.

Lugar de celebración: Castelo Branco (Portugal) Fecha: 24-28 de septiembre de 2011

Autores: Ortega M.F., **Elío J.**, Caballero J., Vaselli O., Nisi B., Giannini L., Grandia F., Vilanova E., Mazadiego L.F., Garcia Gonzalez J.E., Garcia Martinez M.J., Llamas J.F., Chacón E.
Título: Estudio de Análogos Naturales de Captura y Almacenamiento de CO_2: Relación Radón (222Rn) - Torón (220Rn)

Tipo de participación: Comunicación Oral
Congreso: VIII Congreso Ibérico de Geoquímica-XVII Semana de Geoquímica

Lugar de celebración: Castelo Branco (Portugal) Fecha: 24-28 de septiembre de 2011

Autores: Nisi B., Vaselli O., **Elío J.**, Tassi F., Ortega M.F., Caballero J., Grandia F., Delgado Huertas A., Mazadiego L.F.
Título: Geochemical monitoring of water discharges and dissolved gases in the CO_2 injection site of Hontomin (Burgos, Spain)

Tipo de participación: Comunicación Oral
Congreso: VIII Congreso Ibérico de Geoquímica-XVII Semana de Geoquímica

Lugar de celebración: Castelo Branco (Portugal) Fecha: 24-28 de septiembre de 2011

Autores: Nisi B., **Elío J.**, Vaselli O., Tassi F., Grandia F., Mazadiego L.F.
Título: Geochemical monitoring in the Hontomín (Burgos, Spain) injection site: preliminary results and perspectives

Tipo de participación: Poster
Congreso: EGU General Assembly 2011

Lugar de celebración: Viena (Austria) Fecha: 3-8 de abril de 2011

Autores: Vaselli O., Nisi B., Tassi F., Mazadiego L.F., **Elío J.**, Ortega M.F., Caballero J., Grandia F., Vilanova E.
Título: Geochemical baseline characterization of the storage area around the injection site at Hontomín (Burgos, Spain)

Tipo de participación: Poster
Congreso: Coloquio Franco-Español, almacenamiento geológico de CO_2

Lugar de celebración: Pau (Francia) Fecha: 22-24 de noviembre de 2010

Autores: Vaselli O., Tassi F., Bicocchi G., Nisi B., Montegrossi G., Burgassi P., Grandia F., **Elío J.,** Bruno J.
Título: Injection and Extraction of CO_2: the role of the Geochemical Monitoring

Tipo de participación: Cominicación Oral
Congreso: IGRS International Geo-Hazards Research Society, Scientific approach to GeoHazard: a window to the future. 2nd Symposium

Lugar de celebración: Rosignano Marittimo (Italia) Fecha: 27 de septiembre de 2010

CAPÍTULO VI: ADDENDUM

1. Introduction

The European Energy Program for Recovery (EEPR) selected in 2009 the OXYCFB300 Compostilla Project (Lupión et al., 2011) as one of the six CCS Demo projects which include a Technology Development phase, where pilot facilities for CO_2 capture, transport and storage will be built and operated, giving a valuable input to the demo phase (European Energy Program for Recovery – EEPR, http://www.compostillaproject.eu). The main goals are the development and optimization of feasible injection strategies, establishment of monitoring methodologies to verify the evolution of the injected CO_2 and assure its safety, investigation and understanding of the long term processes that control CO_2 geological storage, to demonstrate the viability of the sequestration and storage of CO_2 to reduce the emissions of this greenhouse gas to the atmosphere and mitigate its potential climate changes.

The storage area of the project is located close to the village of Hontomín (Burgos, northern Spain) where approximately 20,000 tons of CO_2 are planned to be injected into a saline aquifer at 1,500 m depth from the end of 2013 and during the following two years. This Technology Development Plant on CO_2 Storage (TDP) is owned and operated by the Fundación Ciudad de la Energía (CIUDEN), which belongs to the Spanish Government.

2. Objectives

The specific objectives of the thesis, in the TDP of Hontomín, were to:

a) establish, for the specific features of the CO_2 storage site, the most suitable way for measuring CO_2 flux and the optimum statistical approach for estimating the total CO_2 output using the accumulation chamber method;

b) define a CO_2 geochemical baseline to be used as background for future monitoring studies, assess the seasonal variability of CO_2 soil flux and evaluated if there are influences in CO_2 flux by differences in geology and land uses;

c) detect a potential outflow of fluids from deep reservoirs through preferential migration pathway of gases, like fault zone or wells;

d) provide a geochemical characterization of the surface and spring water discharges to assess the main geochemical processes that affect the shallow hydrogeological system, propose a geochemical approach to ascertain the origin of CO_2 in the dissolved gases prior the injection and suggest which geochemical and isotopic parameters can be regarded as suitable tracers of CO_2 leakages at the near-surface;

e) apply different monitoring techniques according to the results obtained via the studies of natural analogues.

In natural analogues, the main aim was to test different techniques and evaluate their applicability in the monitoring of CO_2 storage, not considering the geochemical characterization of the emission sites. Thus, the specifics objectives were to:

a) establish, for the specific features of the CO_2 analogue, the most suitable way for measuring CO_2 flux and the optimum statistical approach for estimating the total CO_2 output using the accumulation chamber method;

b) investigate the relation between the radon isotope activity and ratios ($^{222}Rn/^{220}Rn$) in soil-gas and CO_2 soil flux, evaluating the characteristics of CO_2 as carrier gas and the effectiveness of radon measurement to discriminate between superficial and deep source of the gas, and therefore the applicability of these measures in monitoring programs related to carbon storage projects.

3. Conclusions

Superficial monitoring methods (e.g. water chemistry and soil-gas) are ones of the most important activities in the monitoring of a geologic storage of carbon dioxide, both at the stage of sites characterization as during the injection and post-injection. These methods allow to detect and quantify the possible leakages of CO_2. After the analysis of different techniques was deduced that:

3.1. Sampling strategies using the "accumulation chamber" for monitoring geological storage of CO_2

Calculating the baseline of diffuse CO_2 soil flux is essential when characterizing a site where this gas is going to be stored underground, in order to detect the possible leakages. In these projects, the flux values are expected to be low and homogeneous. And if leakages occur, small variation in CO_2 flux must be detected with a high CO_2 "noise" from biological activity (soil respiration). Thus, it is important to obtaining the most accurate CO_2 flux values.

For this reason it was decided to carry out geochemical surveys by using the best methodology presently available for measuring the flux of CO_2, i.e. the accumulation chamber method. The measurement protocol was tested comparing three different approaches: (a) prior clearance of the area on which the chamber is to be placed and then immediately sampling (CM); (b) not clearing the area, independently by the presence of any vegetative cover (nCM) and (c) clearing the area and wait for about 1h before measuring (CWM).

After performing a statistical analysis (Mixed Linear Model), we concluded that the method chosen was significantly affecting the measured CO_2 flux value. The highest values were recorded when the CM approach was used. This is likely due to the fact that the top layer of the ground was importantly disturbed during clearance, causing a temporary leakage of soil gas and the subsequent overestimation of the emission value.

The results indicated that sampling could better be performed without clearance (nCM) or after clearance and waiting (CWM). However, the results obtained after clearance and waiting (CWM) show less dispersion, suggesting that CMW is the best technique for monitoring CO_2 Storage sites.

3.2. Statistical approach for estimating the total CO_2 emission rate using the "accumulation chamber" method

Partitioning of CO_2 flux data into different log-normal populations may help to distinguish among different geochemical processes, e.g. geological or biological sources of CO_2. Thus, this approach is an important tool in monitoring programs of CCS, where the main goals are to demonstrate that there are not leakages from the reservoir to the atmosphere and if it occurs detect and quantify. In this sense, the partitioning of populations is best done with maximum likelihood criteria. Since with graphical procedure, although described by Sinclair (1974), have a relative high degree of subjectivity in the interpretation and the results may not be reproducible.

The estimation methods MA, MVUE, bootstrap, ML and Sinclair, are based on independent data. Thus, if these data are correlated and a variogram model can be fitted to explain this relationship among them, these methods are not appropriated. In these cases, geostatistical techniques (sGs) have a more robust estimation value.

Therefore, the first step to estimate the total emission rate, once anomalous values are detected, is to make a variogram analysis. If the relation between the data can be explained with the variogram, the best technique to calculate the total CO_2 output and its confidence interval is the sequential Gaussian simulation method (sGs). If data are independent (no variogram), the distribution of the data is to be analyzed. For normal and log-normal distributions the proper methods are the arithmetic mean and MVUE, respectively. If the data are not normal (log-normal) or are a mixture of population the best method is the bootstrap resampling.

Following these steps, the maximum confidence interval was about ±20/25%, with most of values varying between ±3.5% and ±8%. These vales are good enough for the CO_2 estimation output, since the error of the instrument is about 25% and the CO_2 flux usually has a high local variation owning to the changes in the ground properties. Therefore, it can be considered an optimal procedure for the application in monitoring and verification program of a geological CO_2 storage site

3.3. Soil-gas radon (^{222}Rn – ^{220}Rn) measurements

The CO_2-rich emissions in the natural analogue of *"Campo de Calatrava"* are mainly associated with fracture systems, although gas leakages as local spots were recognized. In some cases, very high values of CO_2 flux (up to 1 $t \cdot m^{-2} \cdot d^{-1}$) were recognized, although at short distances from the main emission point, i.e. 3 to 5 m (or even smaller, at the scale of few decimeters), abrupt decreases, down to typical values for biologic fluxes, were recorded. This observation, when transferred to CO_2 storage sites, allows to understand the difficulties that may be faced during monitoring programs since the release of CO_2, if any, to the atmosphere may occur at a large temporal scale.

In all emission zones, an increase of ^{222}Rn concentration in soil-gas was detected and was correlated to the CO_2 flux. The influence of this ^{222}Rn anomaly zone, though small, seems to be higher than that of CO_2. Consequently, Rn may be considered as a good tracer to discriminate a leakage zone. In this sense, the radon measurement can be used as a tool to study the CO_2 migration, and able to discriminate between biological and deep origin, possibly defining the area of leakage.

It has been verified that the increase of ^{222}Rn in the soil-gas may be produced by two mechanisms, i) direct transport by a gas carrier (CO_2) and ii) generation at shallow level due to the increase of U and Ra ratio, as their mobility is favored by carbonated waters. However, more data are necessary to confirm this observation.

The results showed that ^{222}Rn concentrations in the soil-gas are occasionally very high, with values up to 430 $kBq \cdot m^{-3}$. This effect must be considerate in the risk assessment of the CO_2 geological storage, if the leakage occurs in residential zones the concentration inside the house may grow up to unacceptable concentrations, being Radon dangerous for the human health. For the above-mentioned reasons, ingestion of water that has suffered CO_2 leakage has to be considered another risk due to the increase in ^{222}Rn, and U and Ra.

The relation of ^{220}Rn with the CO_2 flux is not straightforth as with ^{222}Rn. In the dry gas vent of "La Sima", a clear ^{220}Rn concentration reduction was detected and related to the CO_2 flux increase. However, in the emission site associated with water springs this relationship was not appreciated, and a slight increase in ^{220}Rn with the CO_2 flux was recorded. This effect seems to be caused by a difference source of the radon isotopes (^{222}Rn – ^{220}Rn), which would possibly suggest the use of radon like a natural tracer. Nevertheless, the feeding (deep?) source of radon needs to be properly investigated.

3.4. CO_2 soil flux baseline at the Technological Development Plant for CO_2 injection at Hontomín

Background CO_2 fluxes at the soil-atmosphere interface in the Hontomín area when the TDP on CO_2 Storage is under construction and will probably be completed at the end of 2013, in the framework of the Compostilla OXYCFB300 project, are low and typical of biological respiration. The average values were between 4.9 and 13 $g \cdot m^{-2} \cdot day^{-1}$, smaller than 18 $g \cdot m^{-2} \cdot d^{-1}$, which may be considered as an upper limit of the arithmetical mean for soil respiration CO_2. Evidences of deep CO_2 inputs (e.g. residual hydrocarbons deposit) were not detected, suggesting that the soil respiration is the only responsible for the observed CO_2 flux at Hontomín.

Measurements were also carried out in zones of preferential ascent of deep fluids, i.e. in the vicinity of i) oil wells (H-1, H-2, H-3 and H-4), ii) ongoing injection and monitoring wells (H-A and H-I) and iii) fault zones (HNT3). The CO_2 soil fluxes in all these areas were very similar to those recorded in undisturbed zones. Only few anomalies (around 40 $g{\cdot}m^{-2}{\cdot}d^{-1}$) near the H-2 oil well were detected. These values cannot be associated with a deep source of CO_2 and it is likely that they are due to an increase in the biological activity. Nevertheless, this zone should be regarded as a potential risk area for leakages during and after the CO_2 injection.

Slightly higher values of the CO_2 flux values were observed during warmer periods as the biological activity increases. Similarly, CO_2 flux was higher in areas where vegetated (cultivated and forestry) areas dominated.

At Hontomín, CO_2 flux is low and homogenously distributed in winter, whereas in warm periods it is heterogeneous and higher due to the increased biological activity. Thus, the detection of possible leakages from the reservoir in CCS projects can more easily be recognized in autumn-winter, during which the “noise” from biologic activity is strongly reduced with respect to that occurring in spring-summer time.

The determination of reference CO_2 flux values above which a possible leakage from the reservoir can be considered realistic may help in monitoring and verification programs during CCS projects. Two groups of CO_2 flux values were then calculated. The first ones (UCL_{50}, 5 $g{\cdot}m^{-2}{\cdot}d^{-1}$) can be referred to non-ploughed areas in autumn-winter and 3.5 and 12 $g{\cdot}m^{-2}{\cdot}d^{-1}$ for ploughed and non-ploughed areas in spring-summer time. These values can be used as an indicator of an increasing CO_2 flux and as a warning of possible early leakage. If these values are exceeded, monitoring programs have to be more exhaustive and frequent to evaluate the evolution of a possible early leakage and associated risks. The second ones are for UCL_{99} of 26 $g{\cdot}m^{-2}{\cdot}d^{-1}$ during autumn-winter in not-ploughed areas and 34 and 42 $g{\cdot}m^{-2}{\cdot}d^{-1}$ for spring-summer in ploughed and not-ploughed areas respectively. Exceeding the estimated 99th percentile upper confidence limit an evidence of leakage can seriously be considered.

Soil CO_2 flux measurements in injection plants are a powerful tool to recognize CO_2 leakage at the near surface and verify the feasibility of the safe storage of the greenhouse gas underground (Klusman 2003a, 2003b, 2005; Klusman et al. 2000). However, prior the injection the geochemical baseline of the CO_2 fluxes is required to establish threshold fluxes to be used as reference values for the forthcoming campaigns as those defined for the Hontomín site.

3.5. Hydrogeochemistry of surface and spring waters in the surroundings of the CO_2 injection site at Hontomín–Huermeces (Burgos, Spain)

In this thesis the very first geochemical and isotopic data for the surface and spring waters from the HH, where a pilot plant will shortly be established to inject pure CO_2, were presented. The chemical and isotopic compositions indicate that the studied waters, characterized by relatively low TDS and a $Ca^{2+}(Mg^{2+})$-HCO^{3-} hydrochemical facies, are fed by meteoric waters circulating along a shallow hydrogeological pattern. Despite the fact that an anthropogenic source of NO_3 was recognized, two springs (namely Fuente Hontomin: FH3 and, at minor extent, Fuente Laguillo: LA1) show clues of a possible contribution by deeper waters as derived by the relatively high concentrations of As, B, Ba and U. Similar geochemical features were also found in the Rio Ubierna for which inputs by more saline waters can be hypothesized. The HH water chemistry is mainly related to water–rock interaction processes that involve the sedimentary units characterizing the HH area, such as dissolution of Ca(Mg)-carbonates driven by conversion of H_2CO_3 in HCO_3^- ion. Thus, calcite is the main Ca-supplier, due to its very high dissolution rate, under far-from-equilibrium conditions, compared to that of Ca-bearing silicates and Al-silicates (e.g. Marini, 2007). The $Ca^{2+}(Mg^{2+})$-HCO_3^- waters are indeed generally compatible with closed-system equilibration with carbonate minerals. A significant anthropogenic contamination seems to affect the HH waters, since particularly high NO_3^- concentrations were found in the springs close to the injection area. The $\delta^{13}C$-CO_2 and $\delta^{13}C$-TDIC indicates a biogenic source for carbon dioxide, which in some cases is the dominant component among the dissolved gases, the latter being commonly characterized atmospheric-derived N_2, O_2 and Ar.

The periodical monitoring (from January 2010 to April 2011) carried out in five spring discharges located in the proximity of the site where CO_2 will be injected have indicated significant variations in terms of absolute concentrations and molar ratios of the main components. The geochemical and isotopic data of the surface and spring waters in the surroundings of HH are relevant since they can be considered as background values when intra- and post-injection monitoring programs will be carried out. As a consequence, main and minor solutes, including the carbonate equilibria, are to be considered if a CO_2 leakage through the cap rock would be occurring. Nevertheless, the recorded presence of an anthropogenic contribution cannot be neglected when computing the effects deriving by a CO2 leakage whenever would be interacting with the shallow aquifer. Trace elements, particularly for those water samples where a deep component was likely be recognized (e.g. FH3, LA1 and Rio Ubierna), appear also suitable for a geochemical monitoring. Nevertheless, chemistry of the dissolved gases, the geochemical modeling and TDIC and δ^{13}CTDIC values were also revealed to be important tracers and should be considered when a geochemical monitoring will be designed. The geochemical conditions currently established would indeed change in an event of CO_2 leaking and be recorded in the shallow groundwater system, modifying the geochemical processes governing the water and dissolved gas composition recognized during this pre-injection phase.

4. Future works

Future works will be focused on:

- Evaluating remote sensing techniques to identify and quantify CO_2 leaks. The *UPM* and *UniFi team* (Ortega et al., 2013) has carried out a specific study in the natural analogue of Campo de Calatrava to verify the applicability of multispectral and hyperspectral observations in the detection of leakages.

- Evaluating other soil-gas measurements as monitoring tools. The difficulty to detect and differentiate between biological and deep CO_2 sources suggests that it is necessary to acquire a large number of parameters. In this respect other gases, such as CH_4, H_2, N_2, Ar and He, may successfully be applied for the leakage detection.

- Comparing different radiometric methods to measure radon isotopes ($^{222}Rn/^{220}Rn$), evaluating the differences between them and considering which provide the best results in the different phases of a storage project (pre-, intra- and post-injection).

ANEXOS

Anexo 1: Documentos requeridos para la mención “Doctor internacional”

UNIVERSITÀ
DEGLI STUDI
FIRENZE

DST
DIPARTIMENTO DI
SCIENZE DELLA TERRA

DIP.TO SCIENZE DELLA TERRA
prot. n. 1134 **del** 7.5.13 **pos.** II/12

Florence 7th of May, 2013

E.T.S. Ingenieros de Minas
Universidad Politécnica de Madrid (UPM),
Calle de Ríos Rosas, 21 - 28003 Madrid, Spain
and
Fundación Ciudad de la Energía (CIUDEN)
Avenida Segunda 2 (Compostilla)
nº 2 - 24404 Ponferrada (Spain)

Dear Sirs,

With the present letter I would like to express my deepest compliments to Mr. Javier de Elio Medina who spent 3 months in our Department in the framework of his PhD program. His stay started on the 13th of February and ended on the 15th of May, 2013. In this period, Mr. Elio could accomplish all the goals he targeted. In particular, he completed two papers. The first one, titled: "*CO_2 soil flux baseline at the CO_2 injection pilot plant of Hontomin (Burgos, Spain)*", was submitted to the International Journal of Greenhouse Gas Control (IF: 5.11), while the second one, titled "*Gas monitoring methodology and application to CSS projects as defined by atmospheric and remote sensing survey in the natural analogue of Campo de Calatrava (Spain)*", the latter being submitted, and already accepted, as extended abstract to the CEST-2013 (13th International Conference on Environmental Science and Technology) to be held in Athens from the 5th to the 7th of September, 2013. Another paper, titled "*Application of different statistical methods for soil CO_2 emission rate in CCS sites*", was almost completed and it will be submitted to Mathematical Geosciences. He also attended two field trips, organized by our department, in the Mt. Amiata area and at Vulcano Island. Both fieldtrips were related water and gas sampling. Mr. Elio could thus learn standard sampling procedures and the modifications adopted by our geochemistry group with particular reference to VOC (Volatile Organic Compounds) in fumarolic gases. In the laboratory, he analyzed several water samples in order to get customized with potentiometric and acidimetric titrations and cation and anion chromatography. He could also learn the main techniques for gas analyses (gas chromatography and gas-mass). His activity was also focused in the understanding the geochemical processes affecting the water composition and in the use of the main tools for water classification and water evolution.

I have to say that it was a pleasure to have Mr. Elio in our department since his stay was highly productive and I enjoyed to have him here since he is highly motivated and enthusiastic about everything related to the research activity. I do really hope Mr. Elio can have other chances to visit our department and work together.

Best regards

Prof. Orlando Vaselli

The Head of the Department of Earth Sciences
Prof. Lorenzo Rook

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POLITÉCNICA

INFORME EXPERTO EXTERNO / EXTERNAL REVIEWER REPORT
(ART. 5B DEL REGLAMENTO DE DEFENSA Y EVALUACIÓN DE LA TESIS DOCTORAL)

Nombre del experto/Name of the reviewer Ronald W. Klusman
Categoría/Position Emeritus Professor
Universidad a la que pertenece/Departmento, University /Department Colorado School of Mines, Department of Chemistry and Geochemistry

Título de la tesis/Title of the Ph.D. Thesis: Estrategias de monitorización de CO_2 y otros gases en los estudios de análogos naturales
Nombre del doctorando que presenta la tesis/Name of the Ph.D. candidate: Javier de Elío Medina

Especificar los motivos que avalan la calidad de la tesis mencionada para su defensa:
Specify reasons endorsing the quality of the above-mentioned thesis for its defense:

POLITÉCNICA

The project was a very thorough and complete baseline determination prior to a future inject in Spain. The investigation included measurements of seasonal variations, land use effects, a sampling variability. Although other researchers have acknowledged the existence of signifi seasonal effects, very few have made actual measurements of its extent.

The project also addressed various methods for determining when an excursion in flux occurs. This is is an important parameter to be determined and will have to be developed for each project area. The local climate determines the natural variability which must be well understood if an excursion in gas flux occurs and can be recognized over natural variat

¿Qué objetivos se han logrado con la tesis presentada?
What are the contributions of the Ph.D. thesis?

The project and its thoroughness demonstrate the complexity of the monitoring program that will be necessary in each future project around the world. Most earlier researchers have made simple measurements in test locations but never in a real project location. They have also not adequately addressed a prootocol that might be applied to detection of leakage when the leakage starts out small in magnitude.

The author has used radon measurements as an effective tool for finding zones of potential future leakage pathways when the actual injection phase of the project begins. Although radon may not originate in the reservoir, if leakage occurs, radon will be carried upward toward the suface where it is readily measured.

The author also has recognized that carbon dioxide leakage will alter the equilibrium state of shallow groundwater. Groundwater composition can also be an effective monitoring tool that takes advantage of natural springs or existing water wells as points to be sampled.

POLITÉCNICA

Originalidad del trabajo:
Originality of the work:

The project has applied methodology developed by others and applied it in a new and more complex location and shows substantial originality in testing of the methodology. The thorough characterisation of an area in a baseline condition is important.

Metodología usada / hipótesis contrastadas:
Metodology used / hypotheses tested :

The project uses gas flux methods to characterise the natural exchange of carbon dioxide between the land surface and the atmosphere. Quantification of this exchange rate and its natural variability is an important contribution. These methods will have to be applied in the future to other projects around the world.

POLITÉCNICA

Observaciones:
Observations:

Measurements of gas exchange between the land surface and the atmosphere were made, quantified, and interpreted in a scientific and statistically sound manner.

Considera que la tesis anteriormente mencionada es apta para su defensa pública?
In consideration of all the above, is the Ph.D. Thesis ready for its defense?

X Si / Yes ☐ No

Firma y fecha
Signature and date
Ronald W. Klusman
Ronald W. Klusman
30 September 2013-09-30

POLITÉCNICA

INFORME EXPERTO EXTERNO / EXTERNAL REVIEWER REPORT
(ART. 5B DEL REGLAMENTO DE DEFENSA Y EVALUACIÓN DE LA TESIS DOCTORAL)

Nombre del experto/Name of the reviewer	BRUNELLA RACO
Categoría/Position	RESEARCHER
Universidad a la que pertenece/Departmento, University /Department: Institut of Geosciences and Earth Resources - National Research Council (CNR) - Italy	

Título de la tesis/Title of the Ph.D. Thesis: Estrategias de monitorización de CO_2 y otros gases en los estudios de análogos
Nombre del doctorando que presenta la tesis/Name of the Ph.D. candidate: Javier de Elío Medina

Especificar los motivos que avalan la calidad de la tesis mencionada para su defensa:
Specify reasons endorsing the quality of the above-mentioned thesis for its defense:

The argument presented in this thesis dials with very current issues with an actual step by step scientific approach. The work done is remarkable for the overall breadth of the multidisciplinary effort, the clarity of the explanation and the amount of data presented. The significance of obtained results have been properly tested and they can be traduced in a efficient monitoring procedure for CO_2 re-injection sites.

¿Qué objetivos se han logrado con la tesis presentada?
What are the contributions of the Ph.D. thesis?

The most significant contribution of the thesis concern the production of a protocol for the proper monitoring of CO_2 injection sites. This aim has been drawn by the comparison of different techniques of mesuring systems and and different methodologies for data processing this approach makes the protocol robust and easy to export in site characterized by different natural settings.

POLITÉCNICA

Originalidad del trabajo:
Originality of the work:

The work presents widely used monitoring techniques and data processing methodologies. The originality of the work lies in combining these different techniques, both measurement systems and data processing, in order to obtain a standard protocol for monitoring of CO2 re-injection sites

Metodología usada / hipótesis contrastadas:
Metodology used / hypotheses tested :

The main objective of this thesis is the development of the best monitoring methodology, both from a technical and economical point of view, to use for proper monitoring future sites of CO2 geological storage and this aim has been completely reached.

Observaciones:
Observations:

With regards to PhD thesis, I would like to underlay that Dr. Javier de Elío Medina has shown a good ability to illustrate his work: all chapters are well presented indicating critical thinking and a very good scientific background. Another positive point is the ability of Dr. de Elío Medina to manage successfully the results derived from the different techniques and methodologies in order to obtain novel and accurate results in the field of his research. Overall, the results of the research can be considered innovative and of great interest, both from the scientific and practical points of view. The multi-disciplinary methodological approach and the comparison of different methodology, followed for developing a standard protocol, makes it very reliable and attractive for proper monitoring of CO2 re-injection site.

Considera que la tesis anteriormente mencionada es apta para su defensa pública?
In consideration of all the above, is the Ph.D. Thesis ready for its defense?

It is with great pleasure to recommend Dr. Javier de Elío Medina to defend his thesis.

X Si / Yes ☐ No

Firma y fecha
Signature and date

Pisa November 30th 2013

Brunella Raco

Anexo 2: Ley 40/2010, de 29 de diciembre, de almacenamiento geológico de dióxido de carbono